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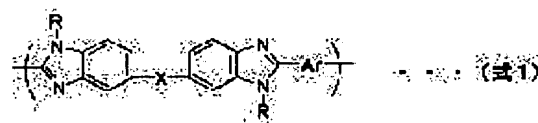
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(54) SULFONIC ACID-CONTAINING ION CONDUCTIVE POLYBENZIMIDAZOLE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polymeric material which enhances the proton conductivity of a polybenzimidazole based polymer having a sulfonic acid group on the aromatic ring and excellent properties such as heat resistance and mechanical properties and, simultaneously, has sufficient water resistance when used as a polymeric electrolyte membrane.

SOLUTION: The sulfonic acid group-containing polybenzimidazole compound has a polymer composed of a repeating unit to be represented by formula (1) [wherein X is selected from -O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, and a direct bond; Ar is selected from aromatic groups containing 0-2 sulfonic groups and contains an average of 0.5 per Ar of the sulfonic acid group; and R is selected from hydrogen, a 2-12C aliphatic group, an aromatic group, an aliphatic/ aromatic substituent, a 2-12C aliphatic sulfonic acid group, an aromatic sulfonic acid group, and an aliphatic/aromatic sulfonic acid substituent] as the major component, has an inherent viscosity, measured in sulfuric acid, of ≥0.1 and, simultaneously, is substantially insoluble in water.



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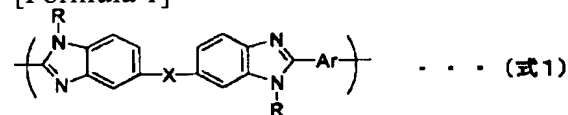
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CLAIMS

[Claim(s)]

[Claim 1] the logarithm which used as the principal component the polymer which consists of a repeat unit expressed with the following general formula (1), and was measured in the sulfuric acid -- the sulfonic group content polybenzimidazole compound characterized by not dissolving in water substantially while viscosity is 0.1 or more.

[Formula 1]



(X is chosen from -O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, and direct coupling among a formula.) Ar is chosen from the aromatic series radical containing 0-2 sulfonic groups, and 0.5 or more sulfonic groups per Ar are contained as the average. R is chosen from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical and the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent.

[Claim 2] The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical in claim 1.

[Claim 3] The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent in claim 1.

[Claim 4] The moldings characterized by using a compound according to claim 1 to 3 as a principal component.

[Claim 5] Film characterized by using a compound according to claim 1 to 4 as a principal component.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to sulfonic group content polybenzimidazole system resin useful as polyelectrolyte film.

[0002]

[Description of the Prior Art] A water electrolyzer and a fuel cell can be raised as an example of the electrochemical equipment which uses a solid polymer electrolyte as an ion conductor instead of a liquid electrolyte. The poly membrane used for these must be chemical, thermal, electrochemical, and dynamic sufficiently stable in proton conductivity as cation exchange membrane. For this reason, as what can be used over a long period of time, the perfluorocarbon-sulfonic-acid film which mainly makes "Nafion (trademark)" by U.S. Du Pont the example of representation has been used. However, if it is going to operate on the conditions exceeding 100 degrees C, membranous water content will fall rapidly, and also it becomes remarkable [membranous softening]. For this reason, in the fuel cell used as a fuel, degradation by the methanol transparency in the film cannot start the methanol with which the future is expected, and sufficient engine performance cannot be demonstrated. Moreover, also in the fuel cell operated near 80 degree C by using as a fuel the hydrogen currently examined by the current Lord, it is pointed out as a failure of establishment of a fuel cell technique that membranous cost is too high.

[0003] In order to conquer such a fault, the polyelectrolyte film which introduced the sulfonic group into the aromatic series ring content polymer is examined variously. For example, they are what sulfonated the poly aryl ether sulfone (Journal of Membrane Science, 83, 211 (1993)), the thing (JP,6-93114,A) which sulfonated the polyether ether ketone, sulfonated polystyrene, etc. However, a desulfonation acid reaction tends to occur with an acid or heat, and the sulfonic group introduced on the ring by using a polymer as a raw material cannot be said to be enough [endurance] for using it as an electrolyte membrane for fuel cells.

[0004] It is possible that the polymer of aromatic series poly azole systems, such as polybenzimidazole, is known as a high heatproof and a polymer of high endurance, a sulfonic group is introduced into these polymers, and it uses for the above-mentioned purpose. As such polymer structure, about the polybenzimidazole containing a sulfonic acid Uno's and others J.Polym.Sci., Polym.Chem., 15, 3 in 1309 (1977), 3'-diaminobenzidine, 3 and 5-dicarboxy benzenesulfonic acid or 4, 6-dicarboxy - what is compounded from 1 and 3-benzene disulfon acid By USP-5312895, it is reported that it is 1, 2, 4, and 5-benzene tetramine which compounds 2 and 5-dicarboxy benzenesulfonic acid as a principal component. However, in these reports, it did not look back about the electrochemical property which sulfonic groups, such as an electrolyte membrane application, have. Therefore, while reconciling thermal resistance, solvent resistance, the mechanical property, and the ionic conduction property, the molecular design which also took workability into consideration further was what is inferior to one of properties at least it not being carried out but using it for the polyelectrolyte film.

[0005] It is reported in USP No. 5,525,436 that the polyelectrolyte film which is excellent in the proton conductivity in the elevated temperature in it sinking a sulfuric acid and a phosphoric acid into polybenzimidazole that polybenzimidazole applies to the polyelectrolyte film on the other hand paying attention to the thermal resistance which it originally has, solvent resistance, a mechanical property, etc. is obtained. Moreover, that to which what is used as a polyelectrolyte by introducing a sulfonic group into polybenzimidazole introduces N-alkyl sulfonic acid into polybenzimidazole is reported by JP,9-73908,A, USP No. 4814399, etc. Moreover, in the collection of macromolecule debate summaries, 49, and P.3217 (2000), the polymer of the structure which also contains N-alkyl chain in coincidence is shown in order to

improve the mechanical strength of N-alkyl sulfonic-acid content polybenzimidazole. Thus, the approach of using as N-alkyl sulfonic acid the attempt which is going to obtain the polyelectrolyte film by introducing a sulfonic group into polybenzimidazole is examined until now, and the examination by what introduced the direct sulfonic group on the aromatic series ring of polybenzimidazole has not been reported. Although the polymer by which the sulfonic group is introduced on the ring of polybenzimidazole with N-alkyl sulfonic-acid structure is reported to USP5,312,876, since the polymer itself is water solubility and it cannot be used from the first as proton conductivity polyelectrolyte film used under moisture existence, the property as polyelectrolyte film is not evaluated in this system.

[0006] As mentioned above, in spite of having expected to excel in the thermal stability higher than other sulfonation poly arylene ether etc. for whether your being Haruka as the sulfonic acid introduced on the ring of polybenzimidazole was shown in J.Polym.Sci., Polym.Chem., 15, and 1309 (1977), it did not inquire in detail as polyelectrolyte film. This reason is considered to be because for it to be restricted in the conductivity of a proton also in electric field in order that the imidazole ring which mainly has the description as the sulfonic group and basic group on a ring may carry out salt formation between intramolecular or a molecule.

[0007]

[Problem(s) to be Solved by the Invention] In case it is used for coincidence as polyelectrolyte film, the purpose of this invention is to obtain polymeric materials with sufficient water resisting property, while raising the proton conductivity of the polybenzimidazole system polymer which has a sulfonic group on a ring with the property excellent in thermal resistance, a mechanical characteristic, etc.

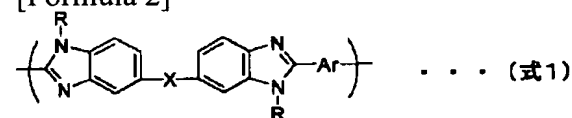
[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of repeating research wholeheartedly, this invention persons can improve a proton conduction property, maintaining a water resisting property by changing the imidazole ring top hydrogen of the polybenzimidazole system polymer containing a specific sulfonic group into a carbon system substituent, and came to get polymeric materials useful as polyelectrolyte film used for a fuel cell etc.

[0009] That is, this invention is attained by following the (1) - (5).

(1) the logarithm which used as the principal component the polymer which consists of a repeat unit expressed with the following general formula (1), and was measured in the sulfuric acid -- the sulfonic group content polybenzimidazole compound characterized by not dissolving in water substantially while viscosity is 0.1 or more.

[Formula 2]



(X is chosen from -O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, and direct coupling among a formula.) Ar is chosen from the aromatic series radical containing 0-2 sulfonic groups, and 0.5 or more sulfonic groups per Ar are contained as the average. R is chosen from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical and the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent.

[0010] (2) The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical in the general formula (1) under above (1).

[0011] (3) The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent in the general formula (1) under above (1).

[0012] (4) The moldings characterized by using the above (1) thru/or the sulfonic group content polybenzimidazole compound in (3) as a principal component.

[0013] (5) Film characterized by using the above (1) thru/or the sulfonic group content polybenzimidazole compound in (4) as a principal component.

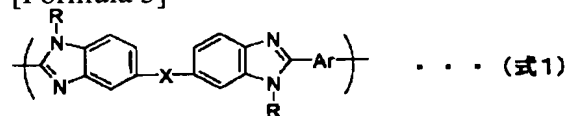
[0014]

[Embodiment of the Invention] This invention is explained to a detail below. With the sulfonic group content polybenzimidazole compound characterized by this invention using as a principal component the polymer which consists of a repeat unit expressed with the following general formula (1) and the moldings

which makes it a principal component, and the film, while excelling in thermal resistance and a mechanical characteristic, the ingredient used as the solid polymer electrolyte having sufficiently high proton conductivity is offered. that logarithm measured in the sulfuric acid in order to use this resin constituent as a polyelectrolyte ingredient -- while viscosity is 0.1 or more, it is necessary not to dissolve in water substantially. a logarithm -- when viscosity is lower than this, problems, like handling becomes difficult arise.

[0015]

[Formula 3]



(X is chosen from -O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, and direct coupling among a formula.) Ar is chosen from the aromatic series radical containing 0-2 sulfonic groups, and 0.5 or more sulfonic groups per Ar are contained as the average. R is chosen from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical and the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent.

[0016] The sulfonic group content polybenzimidazole compound shown by the above-mentioned general formula (1) is the approach which is indicated by JP,9-73908,A and USP No. 4814399 to the polybenzimidazole which has a sulfonic group on a ring, and after it transposes imidazole ring nitrogen top hydrogen to Na, Li, etc., it can be obtained by making it react with alkyl bromide and aprotic solvents. As R in the above-mentioned formula (1), specifically a methyl group, an ethyl group, n-propyl group, n-butyl, n-pentyl radical, n-hexyl group, n-heptyl radical, n-octyl radical, n-nonyl radical, n-decyl group, n-undecyl radical, Straight chain alkyl groups, such as n-dodecyl, an isopropyl group, an isobutyl radical, 2-methylpropyl radical, sec-butyl, tert-butyl, an isopentyl radical, Although aliphatic series / aromatic substitution radicals, such as aromatic series radicals, such as branch-type alkyl groups including an iso hexyl group and 2-methyl pentyl radical, a phenyl group, a naphthyl group, and a toluyl radical, and benzyl, are raised, it is not limited to these. Moreover, some hydrogen atoms on these substituents may be changed by other substituents, such as a hydroxyl group and a halogen radical, and the element. As an example as R, moreover, a methylsulfonic acid radical, 2-ethyl sulfonic group, 3-propyl sulfonic group, 4-butyl sulfonic group radical, 5-pentyl sulfonic group, 6-hexyl sulfonic group, 7-heptyl sulfonic group, 8-octyl sulfonic group, 9-nonyl sulfonic group, 10-DESHIRU sulfonic group, 11-undecyl sulfonic group, Alkyl sulfonic groups, such as 12-dodecyl sulfonic group, 4-phenyl sulfonic group, Although sulfonic group content aliphatic series / aromatic substitution radicals, such as aromatic series sulfonic groups, such as 3-phenyl sulfonic group, a naphthyl sulfonic group, and a toluyl sulfonic group, and a benzyl sulfonic group, are raised, it is not limited to these. These substituents are mixable and can also make not only one sort but two or more substituents exist. As for these substituents, it is desirable to have permuted 30% or more of the hydrogen on imidazole ring nitrogen. When fewer than this, it becomes difficult to demonstrate the engine performance which was excellent in proton conductivity.

[0017] Generally the sulfonic group in the sulfonic group content polybenzimidazole compound of this invention which introduced the above-mentioned N-substituent is obtained in the form of salts, such as Li and Na. In order to remove this salt, the acid treatment generally performed can be used. An acid solution may be made to contact by the solid state of polymer powder, a film, etc., and after dissolving a polymer in an acid solvent, it may supply in a non-solvent and you may collect as a free sulfonic acid type polymer. It is also useful to consider as a free sulfonic acid by mild neutralization using ion exchange resin.

[0018] The polybenzimidazole which has a sulfonic group on the ring which performs above-mentioned N-substitution reaction 3, 3' (-diaminobenzidine, and '3, 3'), 4, and 4'-tetra-amino diphenylsulfone, 2 and 2'-screw (3, 4-diamino phenyl) propane, 2, and 2'-screw (3, 4-diamino phenyl) hexafluoropropane, 3, 3', 4, and 4'-tetra-amino diphenyl ether, It can obtain by the polymerization which combined the aromatic series dicarboxylic acid which does not contain the aromatic series dicarboxylic acid and the sulfonic group containing the aromatic series tetramine chosen from screw (3, 4, -diamino phenoxy) benzene, or its derivative and sulfonic group. As an example of the derivative of the above-mentioned aromatic series tetramine, a salt with acids, such as a hydrochloric acid, a sulfuric acid, and a phosphoric acid, etc. can be raised. Two or more tetramine compounds can also be used not only for an one-sort chisel but for coincidence. These aromatic series tetramines may contain well-known antioxidants, such as chlorination tin

(II) and a phosphorous acid compound, if needed.

[0019] Although above-mentioned sulfonic group content dicarboxylic acid can choose the thing containing one piece or two sulfonic groups into aromatic series system dicarboxylic acid As an example, for example 2, 5-dicarboxy benzenesulfonic acid, 3, 5-dicarboxy benzenesulfonic acid, 4, 6-dicarboxy - 1, 3-benzene disulfon acid, 2, 5-dicarboxy - 1, 4-benzene disulfon acid, 4, 4'-dicarboxy - Sulfonic-acid content dicarboxylic acid and these derivatives, such as 2 and a 2'-biphenyl disulfon acid, can be mentioned. As a derivative, alkali-metal salts, such as sodium and a potassium, ammonium salt, etc. can be raised. Especially the structure of sulfonic group content dicarboxylic acid is not limited to these. Sulfonic group content dicarboxylic acid can be introduced in the form of copolymerization with the dicarboxylic acid which does not contain not only independent [these] but a sulfonic group. Although especially the purity of the dicarboxylic acid containing a sulfonic group is not restricted, it is desirable, and is more desirable. [99% or more of] [98% or more of] Since the inclination for a degree of polymerization to become low is seen compared with the case where the dicarboxylic acid which does not contain a sulfonic group is used for the polybenzimidazole by which the polymerization was carried out by using the dicarboxylic acid containing a sulfonic group as a raw material, as for the dicarboxylic acid containing a sulfonic group, it is desirable to use what has purity high as much as possible.

[0020] As an example of dicarboxylic acid which can be used with the above-mentioned sulfonic group content dicarboxylic acid, the common dicarboxylic acid reported as a polyester raw material, such as terephthalic-acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl ether dicarboxylic acid, diphenylsulfone dicarboxylic acid, biphenyl dicarboxylic acid, terphenyl dicarboxylic acid, 2, and 2-screw (4-carboxyphenyl) hexafluoropropane, can be used, and it is not limited to what was illustrated here. When using the dicarboxylic acid which does not carry out sulfonic group content with the dicarboxylic acid containing a sulfonic group, a sulfonic group needs to contain 0.5 or more per Ar in the above-mentioned formula (1) as the average.

[0021] The polybenzimidazole which has a sulfonic group on the ring which performs above-mentioned N-substitution reaction is compoundable with dehydration and cyclopolymerization which use as a solvent polyphosphoric acid which is indicated by J.F.Wolfe, Encyclopedia of Polymer Science and Engineering, 2nd Ed., Vol.11, and P.601 (1988) in for example, a tetra-amine monomer and a dicarboxylic acid monomer. Moreover, the polymerization by the same device which used methansulfonic acid / phosphorus-pentaoxide mixed solvent system instead of polyphosphoric acid is also applicable. Otherwise, it considers as precursor polymers, such as polyamide structure, at the reaction of the inside of a suitable organic solvent, or mixed monomer melt, and the approach of changing into the target polybenzimidazole structure by the ring closure by suitable subsequent heat treatment etc. can be used. In order to compound the high polymer of thermal stability, the polymerization using the polyphosphoric acid generally used often is desirable. However, in the polymerization to which long duration which is conventionally reported in the polymerization using the dicarboxylic acid which contains a sulfonic group like this invention was applied, there is a possibility that the thermal stability of the obtained polymer may fall. For this reason, although it cannot generally ***** in this invention since polymerization time amount has the optimal time amount with the combination of each monomer, it is desirable to shorten polymerization time amount effectively. By this, a polymer with many amounts of sulfonic groups can also be obtained in the high condition of thermal stability.

[0022] The sulfonic group content poly azole compound of this invention can be extruded from a polymerization solution or the isolated polymer, and can be fabricated by the approach of arbitration, such as spinning, rolling, and the cast, on fiber or a film. It is desirable to fabricate from the solution which dissolved in the suitable solvent especially. Although a suitable thing can be chosen from strong acid [, such as a non-proton polar solvent, and polyphosphoric acid, methansulfonic acid, a sulfuric acid, trifluoroacetic acid,], such as N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, and a hexa methyl HOSUHON amide, as a dissolving solvent, it is not limited to these. Plurality may be mixed and used for these solvents in the possible range. Moreover, it is good as a means which raises solubility also considering what added Lewis acid, such as a lithium bromide, a lithium chloride, and an aluminum chloride, to the organic solvent as a solvent. As for the polymer concentration in a solution, it is desirable that it is 0.1 - 30% of the weight of the range. If too low, a moldability will get worse, and if too high, workability will get worse.

[0023] The method of acquiring a Plastic solid from a solution can use a well-known approach. For example, by immersion to the polymer non-solvent with which it can mix with the solvent which dissolves heating, reduced pressure drying, and a polymer etc., a solvent can be removed and the Plastic solid of

sulfonic group content polybenzimidazole can be acquired. When a solvent is an organic solvent, it is desirable to make a solvent distill off by heating or reduced pressure drying. When a solvent is strong acid, being immersed in water, a methanol, an acetone, etc. is desirable. Under the present circumstances, it can also fabricate in the form compounded with other polymers if needed on fiber or a film. When it combines with the poly bends azole system polymer to which soluble behavior is similar, it is convenient for carrying out good shaping.

[0024] The desirable approach of fabricating the film which uses the sulfonic group content polybenzimidazole compound of this invention as a principal component is the cast from a solution. A solvent can be removed from the solution which carried out the cast as mentioned above, and the film of sulfonic group content polybenzimidazole can be obtained. It is desirable from membranous homogeneity to perform removal of a solvent by desiccation. Moreover, in order to avoid decomposition and deterioration of a polymer and a solvent, it is desirable to dry at the lowest possible temperature under reduced pressure. A glass plate, a Teflon (trademark) plate, etc. can be used for the substrate which carries out the cast. When the viscosity of a solution is high, if a substrate and a solution are heated and the cast is carried out at an elevated temperature, the viscosity of a solution can fall and the cast can be carried out easily. Although especially the thickness of the solution at the time of carrying out the cast is not restricted, it is desirable that it is 10-1000 micrometers. When too thin, it becomes impossible to maintain the gestalt as film, and the uneven film will become easy to be made if too thick. It is 100-500 micrometers more preferably. The approach of controlling the cast thickness of a solution can use a well-known approach. For example, using an applicator, a doctor blade, etc., it can be made fixed thickness, or cast area can be fixed using a glass petri dish etc., and thickness can be controlled by the amount and concentration of a solution. The solution which carried out the cast can obtain the more uniform film by adjusting the removal rate of a solvent. For example, when heating, in the first phase, it can be made low temperature and a vapor rate can be lowered. Moreover, when immersed in non-solvents, such as water, it is suitable in air and inert gas, time amount neglect of the solution is carried out, and the coagulation rate of a polymer can be adjusted. Although the film of this invention can be made into the thickness of arbitration according to the purpose, from an ion conductivity field, a thing thin as much as possible is desirable. It is desirable that it is specifically 200 micrometers or less, it is still more desirable that it is 50 micrometers or less, and it is most desirable that it is 20 micrometers or less.

[0025] Since the phosphonic acid radical of this invention or the sulfonic group content polybenzimidazole polymer is excellent in ion conductivity, it is suitable also for making it the shape of a film and film and using it as ion exchange membrane, such as a fuel cell. Furthermore, it can also use by using polymer structure of this invention as a principal component as coatings, such as binder resin when producing the zygote of the ion exchange membrane of this invention, and an electrode.

[0026]

[Example] Although this invention is concretely explained using an example below, this invention is not limited to these examples. In addition, various measurement was performed as follows.

a logarithm -- viscosity: -- polymer powder -- the concentration of 0.5g/dl -- concentrated sulfuric acid -- dissolving -- the inside of a 30-degree C thermostat -- an Ostwald viscometer -- using -- measurement of viscosity -- carrying out -- a logarithm -- viscosity $[\ln(ta/tb)]/c$ estimated (for the number of fall seconds of the sample solution, and t_b , the number of fall seconds of only a solvent and c are [ta] polymer concentration).

ion conductivity measurement: -- the probe (product made from polytetrafluoroethylene) top for its original work measurement -- the front face of a strip-of-paper-like film sample -- a platinum wire (diameter: 0.2mm) -- pressing -- the constant temperature of 80-degree-C95%RH -- the inside of - constant humidity oven (Nagano Science Equipment Mfg. Co., Ltd., LH-20-01) -- a sample -- holding -- the alternating current impedance between platinum wires -- SOLARTRON1250FREQUENCY RESPONSE It measured by ANALYSER. The distance between electrodes was changed, it measured and the conductivity which canceled the contact resistance between the film and a platinum wire by the following formulas from the distance between electrodes and the inclination which plotted the resistance measurement value calculated from the Cole-Cole plot was computed.

Conductivity [S/cm] Inclination between = $1/[\text{film width cm}] \times [\text{thickness cm}] \times \text{resistance poles}$ [omega/cm]

IR measurement: It measured with the micro transmission method which used Biorad company FTS-40 for the spectroscopy and used BioradUMA-300A for the microscope.

NMR measurement: Varian company Unity-500 were used for the spectroscopy and H-NMR was measured

at DMSO-d₆ and the measurement temperature of 80 degrees C to the solvent.

[0027] It is a temperature up to 100 degrees C, measuring an example 13, 3', and 4 and 4'-tetra-amino diphenylsulfoneg [1.500] (5.389x10⁻³mole) and 2 and 5-dicarboxy benzenesulfonic acid monosodium (99% of purity) 1.445g (5.389x10⁻³mole), 20.48g (75% of phosphorus-pentaoxide contents) of polyphosphoric acid and 16.41g of phosphorus pentaoxides in a polymerization container, and agitating nitrogen slowly on a sink and an oil bath. It carried out. It is a temperature up to 150 degrees C after holding at 100 degrees C for 1 hour. It carries out and is a temperature up to 1 hour and 200 degrees C. The polymerization was carried out and carried out for 3 hours. It cooled radiationally after polymerization termination, water was added, the polymerization object was taken out, and rinsing was repeated until it became pH-indicator-paper neutrality using the home mixer. Reduced pressure drying of the obtained polymer was carried out at 80 degrees C all night. the logarithm of a polymer -- viscosity showed 1.52. Obtained polymer 500mg (1.11x10⁻³mole) was put into the glass reaction container, and the vacuum drying was carried out on 100-degree-C oil bath (about 3 hours). Dimethylacetamide (DMAc) 10ml was added here and it was made to dissolve in it at 150 degrees C. After lowering a system to 70 degrees C, 41mg (5.16x10⁻³mole) of lithium hydrides was added, bromination propyl 4.66ml (= 6.3g) (5.12x10⁻²mole) was added after 90-minute churning, reaction temperature was made into 80 degrees, and the reaction was continued for 3 hours. After diluting with N-methyl pyrrolidone (NMP), the white polymer was made to reprecipitate in 150ml THF after radiationnal cooling. Since the sulfonic acid of a product served as Li salt, in order to consider as a free acid, it remelted the generation polymer to methansulfonic acid, and made it reprecipitate underwater. the logarithm of the obtained polymer -- viscosity showed 0.97. The IR spectrum of the obtained polymer is shown in drawing 1 . H-NMR showed that 75% of the imidazole ring nitrogen top hydrogen in a polymer was permuted by the propyl group (drawing 2). The cast of the N-propyl-ized polymer was carried out on the glass plate from the NMP solution, and it produced the film. Even if it processed the desiccation film with 80-degree C hot water for 1 hour, when it is changeless in the gestalt of a film and this was made into the test portion, the ionic conductivity in 80-degree-C95%RH showed cm in 0.00051S /.

[0028] It sets in the example 2 example 1, and is a polymer. N-propyl sulfonic-acid compound was obtained using 300mg (6.63x10⁻⁴mole), 21mg (2.64x10⁻³mole) of lithium hydrides, DMAc10ml, and propane ape ton 3.23g (2.64x10⁻²mole). the logarithm of the obtained polymer -- viscosity showed 0.57. The IR spectrum of the obtained polymer is shown in drawing 3 . H-NMR showed that 90% of the imidazole ring nitrogen top hydrogen in a polymer was permuted by the propyl sulfonic group. Even if it carried out hot water processing like the example 1, it is changeless in the gestalt of a film and the measured ionic conductivity showed cm in 0.06S /.

[0029] When the film was produced without carrying out N-substitution reaction and ionic conductivity was measured like the example 1 about the polymer which carried out the polymerization in the example of comparison 1 example 1, cm was shown in 0.00019S /.

[0030]

[Effect of the Invention] It can succeed in raising the proton conductivity of the polybenzimidazole system polymer which has a sulfonic group on the ring which has the property excellent in thermal resistance, a mechanical characteristic, etc. by this invention, and the ingredient in which it also considers as polyelectrolytes, such as a fuel cell, and the engine performance which was ** is shown can be offered.

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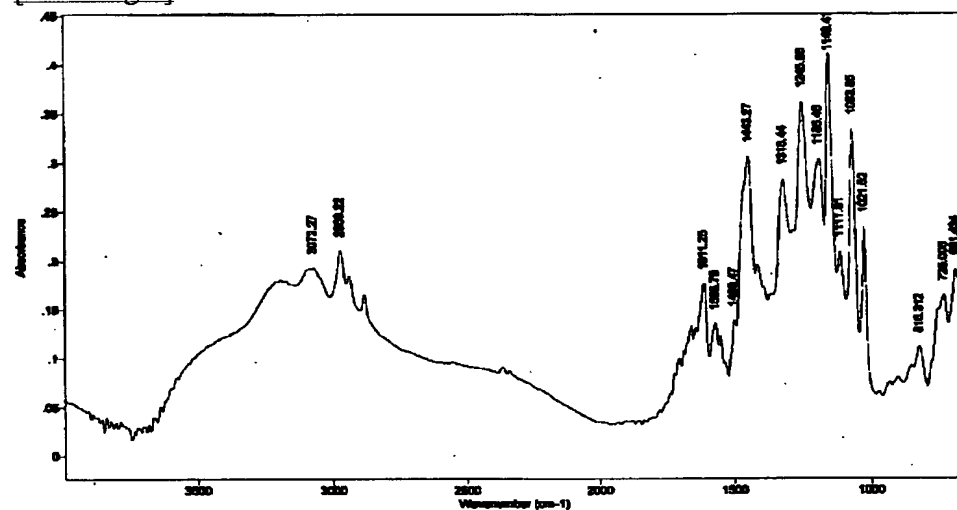
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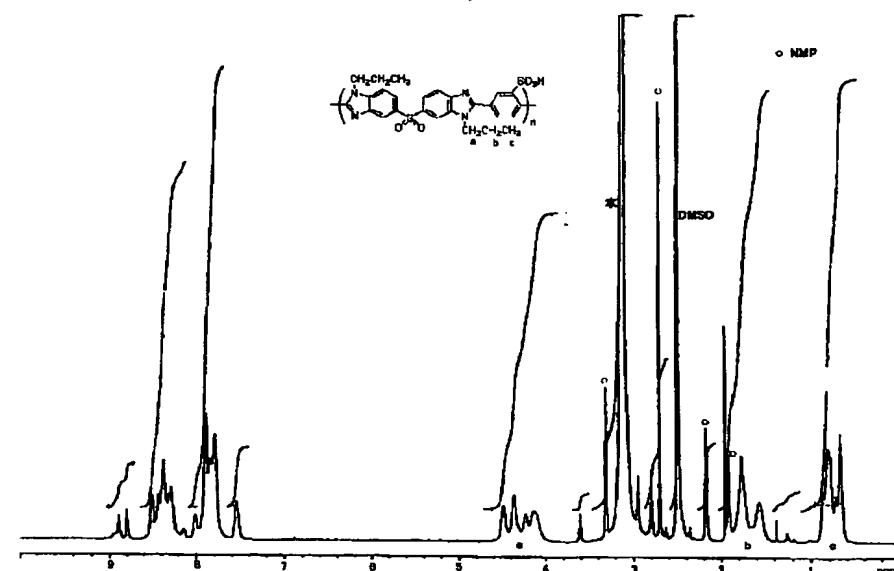
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DRAWINGS

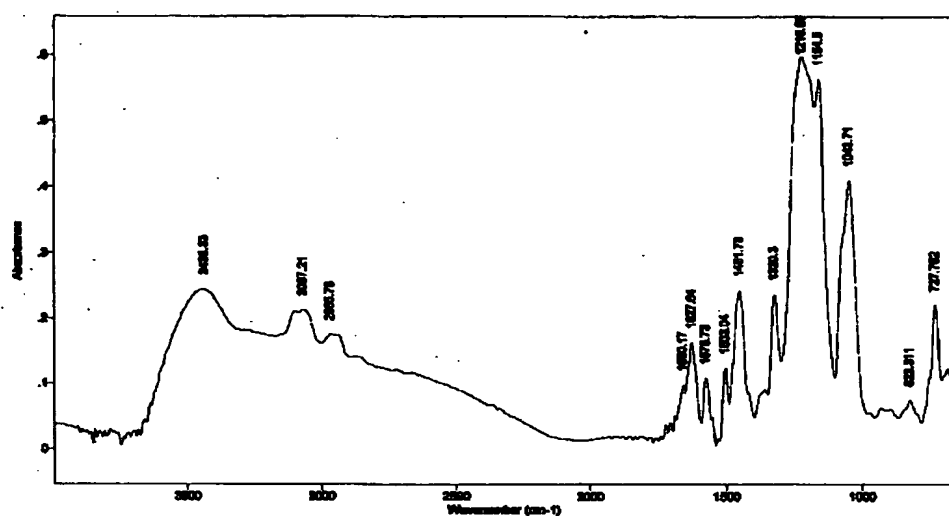
[Drawing 1]



[Drawing 2]



[Drawing 3]



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PATENT ABSTRACTS OF JAPAN

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(54) SULFONIC ACID-CONTAINING ION CONDUCTIVE POLYBENZIMIDAZOLE

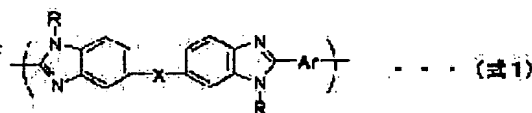
(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polymeric material which enhances the proton conductivity of a polybenzimidazole based polymer having a sulfonic acid group on the aromatic ring and excellent properties such as heat resistance and mechanical properties and, simultaneously, has sufficient water resistance when used as a polymeric electrolyte membrane.

SOLUTION: The sulfonic acid group-containing polybenzimidazole compound has a polymer composed of a repeating unit to be represented by formula (1)

[wherein X is selected from -O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, and a direct bond; Ar is selected from aromatic groups containing 0-2 sulfonic groups and contains an average of 0.5 per Ar of the sulfonic acid group; and R is selected from hydrogen, a 2-12C aliphatic group, an aromatic group, an aliphatic/ aromatic substituent, a 2-12C aliphatic sulfonic acid group, an aromatic sulfonic acid group, and an aliphatic/aromatic sulfonic acid substituent] as the major component, has

an inherent viscosity, measured in sulfuric acid, of ≥ 0.1 and, simultaneously, is substantially insoluble in water.



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審査請求 未請求	請求項の数 5	OL	8/10

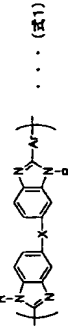
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(54)【発明の名称】	スルホン酸含有イオン伝導性ポリベンズイミダゾール	最終頁に続く
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【要約】 耐熱性、機械特性など優れた性質を持つ芳香環上にスルホン酸基を持つポリベンズイミダゾール系ポリマーのプロトン伝導性を高めるとともに、同時に高分子電解質膜として使用する際に十分な耐水性をもつ高分子材料を得ることにある。

【解決手段】 下記一般式(1)で表される繰り返し単位からなる重合体を主成分とし、硫酸中で測定した対数粘度が0.1以上であるとともに実質的に水に溶解しないことを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【化1】

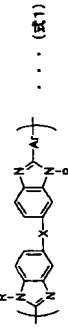


(式中、Xは-O-、-SO₂-、-C(CH₃)₂-、-C(CF₃)₂-、-OPhO-、直接結合から選ばれる。Arはスルホン酸基を0〜2個含む芳香族基から選ばれ、平均値としてスルホン酸基はArあたり0.5個

【特許請求の範囲】

【請求項1】 下記一般式(1)で表される繰り返し単位からなる重合体を主成分とし、硫酸中で測定した対数粘度が0.1以上であるとともに実質的に水に溶解しないことを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【化1】



(式中、Xは-O-、-SO₂-、-C(CH₃)₂-、-C(CF₃)₂-、-OPhO-、直接結合から選ばれる。Arはスルホン酸基を0〜2個含む芳香族基から選ばれ、平均値としてスルホン酸基はArあたり0.5個以上含まれる。Rは水素、炭素数2〜12個の脂肪族、芳香族、脂肪族/芳香族置換基および炭素数2〜12個の脂肪族スルホン酸、芳香族スルホン酸、脂肪族/芳香族スルホン酸置換基から選ばれる。)

【請求項2】 請求項1においてRが水素、炭素数2〜12個の脂肪族、芳香族、脂肪族/芳香族置換基から選ばれることを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【請求項3】 請求項1においてRが水素、炭素数2〜12個の脂肪族スルホン酸、芳香族スルホン酸、脂肪族/芳香族スルホン酸置換基から選ばれることを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【請求項4】 請求項1乃至3のいずれかに記載の化合物を主成分とすることを特徴とする成形物。

【請求項5】 請求項1乃至4のいずれかに記載の化合物を主成分とすることを特徴とする膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、高分子電解質膜として有用なスルホン酸基含有ポリベンズイミダゾール系樹脂に関するものである。

【0002】

【従来の技術】 液体電解質のかわりに高分子固体電解質をイオン伝導体として用いる電気化学的装置の例として、水電解槽や燃料電池を上げることができる。これらに用いられる高分子膜は、カチオン交換膜としてプロトン伝導率とともに化学的、熱的、電気化学的および力学的に十分安定なものでなくてはならない。このため、最も期待にわたる使用できるものとしては、主に米デュポン社の「ナフイオン(登録商標)」を代表例とするパーフルオロポリイミド膜が使用されてきた。しかしながら、100℃を超える条件で運転しようとするとき、膜の含水率が急激に落ちるほか、膜の軟化も顕著となる。このため、将来が期待されるメタノールを燃料とする燃料電池においては、膜内のメタノール透過による性能低下がおこり、十分な性能を発揮することはできない。また、現在主に検討されている水系を燃料として80℃付近で運転する燃料電池においても、膜のコストが高すぎることを燃料電池技術の確立の障害として指摘されている。

【0003】 このような欠点を克服するため、芳香族環含有ポリマーにスルホン酸基を導入した高分子電解質膜が種々検討されている。例えば、ポリアリールエーテルスルホン酸をスルホン化したもの(Journal of Membrane Science, 83, 211(1993))、ポリエーテルエーテルアクトンをスルホン化したもの(特開平6-93114号)、スルホン化ポリスチレン等である。しかしながら、ポリマーを原料として芳香環上に導入されたスルホン酸基は酸または熱により脱スルホン酸反応が起こりやすく、燃料電池用電解質膜として使用するには耐久性が十分であるとは言えない。

【0004】 高耐熱、高耐久性のポリマーとしてはポリベンズイミダゾールなどの芳香族ポリアゾール系のポリマーが知られており、これらのポリマーにスルホン酸基を導入して上記目的に利用することが考えられる。このようなポリマー構造として、スルホン酸を含有したポリベンズイミダゾールについては、UnoらのJ. Polym. Sci. i, Polym. Chem., 15, 1309(1977)における3, 3'-ジアミノベンズジンと3, 5-ジカルボキシベンゼンズルホン酸または4, 6-ジカルボキシ-1, 3-ベンゼンジスルホン酸から合成するものが、USP-5312895では1, 2, 4, 5-ベンゼンテトラミンと2, 5-ジカルボキシベンゼンズルホン酸を主成分として合成するものが報告されている。しかし、これらの報告では、電解質膜用途などスルホン酸基が持つ電気化学的特性、耐溶剤性、機械的特性とイオン伝導特性を両立させることともに、さらに加工性をも考慮した分子設計は行われておらず、高分子電解質膜などには使用するには少なくともいづれかの特性に劣るものであった。

【0005】 一方、ポリベンズイミダゾールが本来持つ耐熱性、耐溶剤性、機械的特性等に注目して、高分子電解質膜に適用することは、例えばポリベンズイミダゾールに硫酸やリン酸を含有することで高温でのプロトン伝導性に優れた高分子電解質膜が得られることがUSP 5, 525, 436号において報告されている。また、ポリベンズイミダゾールにスルホン酸基を導入することで高分子電解質とするものは、ポリベンズイミダゾールにN-アルキルスルホン酸を導入するものが特開平9-73908号やUSP 4814399号等で報告されている。また、高分子討論会要旨、49, p. 3217(2000)においては、N-アルキルスルホン酸含有ポリベンズイミダゾールの機械強度を改善する目的でN-アルキル類も同時に含有する構造のポリマーが示されている。このように、ポリベンズイミダゾールにスルホ

ン酸基を導入することで高分子電解質膜を得ようとする試みは、N-アルキルスルホン酸とする方法がこれまで検討されてきており、ポリベンズイミダゾール芳香族環上に直接スルホン酸基を導入したものの検討は報告されてきていない。N-アルキルスルホン酸構造を持つポリベンズイミダゾールの芳香環上にスルF₅、3,12,入された報告されているが、ポリマー自体が水溶性であるために水分存在下で使用されるプロトン伝導性分子電解質膜としてはともと使用できるものではないの、この系においても高分子電解質膜としての特性は評価されている。

【0006】以上のように、ポリベンズイミダゾールの芳香環上に導入されたスルホン酸は、Polym. Sci., Polym. Chem., 15, 1309(1977)に示されているように、他のスルホン化ポリアリーレンエーテルなどより遙かに高い熱安定性に優れていることが期待されるにもかかわらず、高分子電解質膜として詳しく検討されることはなかった。この理由は、主には芳香環上のスルホン酸基と塩基性としての特徴を持つイミダゾール環が分子内あるいは分子間で塩形成をするために、電界内においてもイオンの伝導性が制限されてしまうことによると考えられる。

【0007】

【発明が解決しようとする課題】本発明の目的は、耐熱性、機械特性など優れた性質を持つ芳香環上にスルホン酸基を持つポリベンズイミダゾール系ポリマーのイミダゾール環を高めてともに、同時に高分子電解質膜として使用する際に十分な耐水性をもつ高分子材料を得ることにある。

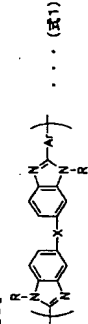
【0008】

【課題を解決するための手段】本発明者らは、上記目的を達成するために鋭意研究を重ねた結果、特定のスルホン酸基を含むポリベンズイミダゾール系ポリマーのイミダゾール環上水素を炭素系置換基に変換することで耐水性を維持しながらプロトン伝導性を改良することができ、燃料電池などに使用する高分子電解質膜として有用な高分子材料を得るに至った。

【0009】すなわち本発明は、下記(1)～(5)により達成される。

(1)下記一般式(1)で表される繰り返し単位からなる重合体を主成分とし、硫酸で測定した対数粘度が0.1以上であるとともに実質的に水に溶解しないことを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【化1】



(式1)

(式中、Xは-O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, 直接結合から選ばれる。Arはスルホン酸基を0～2個含む芳香族基から選ばれる。平均値としてスルホン酸基はArあたり0.5個以上含まれる。Rは水素、炭素数2～12個の脂肪族、芳香族、脂肪族/芳香族置換基および炭素数2～12個の脂肪族スルホン酸、芳香族スルホン酸、脂肪族/芳香族スルホン酸置換基から選ばれる。)

【0010】(2)下記(1)中の一般式(1)においてRが水素、炭素数2～12個の脂肪族、芳香族、脂肪族/芳香族置換基から選ばれることを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【0011】(3)下記(1)中の一般式(1)においてRが水素、炭素数2～12個の脂肪族スルホン酸、芳香族スルホン酸、脂肪族/芳香族置換基から選ばれることを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物。

【0012】(4)下記(1)乃至(3)におけるスルホン酸基含有ポリベンズイミダゾール化合物を主成分とすることを特徴とする成形物。

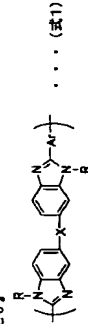
【0013】(5)下記(1)乃至(4)におけるスルホン酸基含有ポリベンズイミダゾール化合物を主成分とすることを特徴とする膜。

【0014】

【発明の実施の形態】以下本発明について詳細に説明する。本発明は、下記一般式(1)で表される繰り返し単位からなる重合体を主成分とすることを特徴とするスルホン酸基含有ポリベンズイミダゾール化合物、およびそれを主成分とする成形物、膜により、耐熱性、機械特性に優れるとともに、十分な高いプロトン伝導性を合わせ持つ高分子固体電解質となる材料を提供するものである。この樹脂組成物は、高分子電解質材料として使用するため、硫酸で測定したその対数粘度は0.1以上であるとともに実質的に水に溶解しないことが必要となる。対数粘度がこれより低い場合、取り扱いが困難になるなどの問題が生じる。

【0015】

【化3】



(式中、Xは-O-, -SO₂-, -C(CH₃)₂-, -C(CF₃)₂-, -OPhO-, 直接結合から選ばれる。Arはスルホン酸基を0～2個含む芳香族基から選ばれる。平均値としてスルホン酸基はArあたり0.5個以上含まれる。Rは水素、炭素数2～12個の脂肪族、芳香族、脂肪族/芳香族置換基および炭素数2～12個の脂肪族スルホン酸、芳香族スルホン酸、脂肪族/芳香族スルホン酸置換基から選ばれる。)

【0016】上記一般式(1)で示されるスルホン酸基含有ポリベンズイミダゾール化合物は、芳香環上にスルホン酸基を持つポリベンズイミダゾールに対して、特開平9-73908号やUSP4814399号に記載されているような方法で、イミダゾール環置換基上水素をN a,1などに置き換えたのち、アルキルプロモリドやサル トン類などと反応させることで得ることができる。上記式(1)中のRとしては、具体的にはメチル基、エチル基、n-プロピル基、n-ブチル基、n-ペンチル基、n-ヘキシル基、n-オクチル基、n-ノニル基、n-デシル基、n-ウンデシル基、n-ドデシル基等の直鎖アルキル基、イソプロピル基、イソブチル基、2-メチルブチル基、sec-ブチル基、tert-ブチル基、イソペンチル基、イソヘキシル基、2-メチルペンチル基をはじめとする分岐型アルキル基、フェニル基、ナフチル基、トリル基等の芳香族基、ベンジル基等の脂肪族/芳香族置換基があげられるがこれらに限定されるものではない。また、これらの置換基上の一部の水素原子が、水酸基、ハロゲン基など他の置換基、元素で置き換わっていても良い。また、Rとしての具体例としては、メチルスルホン酸基、2-エチルスルホン酸基、3-プロピルスルホン酸基、4-ブチルスルホン酸基、5-ペンチルスルホン酸基、6-ヘキシルスルホン酸基、7-ヘプチルスルホン酸基、8-オクチルスルホン酸基、9-ノニルスルホン酸基、10-デシルスルホン酸基、11-ウンデシルスルホン酸基、12-ドデシルスルホン酸基等のアルキルスルホン酸基、4-フェニルスルホン酸基、3-フェニルスルホン酸基、ナフチルスルホン酸基、トリルスルホン酸基等の芳香族スルホン酸基、ベンジルスルホン酸基等のスルホン酸基含有脂肪族/芳香族置換基等もあげられる。

【0017】上記N-置換基を導入した本発明のスルホン酸基含有ポリベンズイミダゾール化合物中のスルホン酸基は、一般にはLiやNa等の塩の形で得られる。この塩をばすには、一般に行われる酸処理を使用することができ、ポリマー粉末、フィルム等の固体状態で酸溶液と接触させても良い。ポリマーを酸溶液に溶解した後非溶媒中に投入してフリーのスルホン酸型ポリマーとして回収しても良い。イオン交換樹脂を用いたマイルドな中和により、フリースルホン酸とすることも有用である。

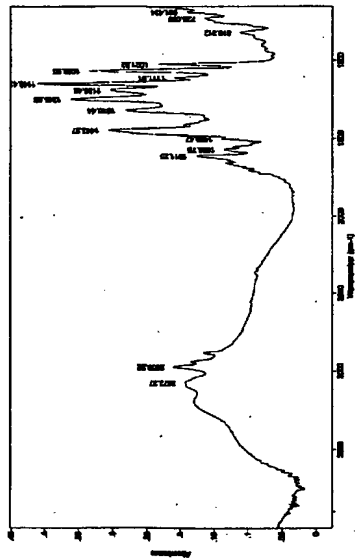
【0018】上述のN-置換反応を行う芳香環上にスルホン酸基を持つポリベンズイミダゾールは、3,3'-ジアミノベンジン、3,3',4,4'-テトラアミノ

ノフェニルスルホン、2,2-ビス(3,4-ジアミノフェニル)プロパン、2,2-ビス(3,4-ジアミノフェニル)ヘキサフルオロプロパン、3,3',4,4'-テトラアミノジフェニルエーテル、ビス(3,4-ジアミノフェニル)ベンゼンから選ばれる芳香族テトラミンまたはその誘導体とスルホン酸基を含む芳香族ジカルボン酸およびスルホン酸基を含む芳香族ジカルボン酸を組み合わせた重合により得ることができる。上記芳香族テトラミンの誘導体の例としては、塩酸、硫酸、リン酸などの酸との塩とをあげることができ、テトラミン化合物は、1種のみだけでなく同時に複数使用することもできる。これらの芳香族テトラミンは、必要に応じて塩化せず(11)や亜リン酸化合物など公知の酸化防止剤を含んでもよい。

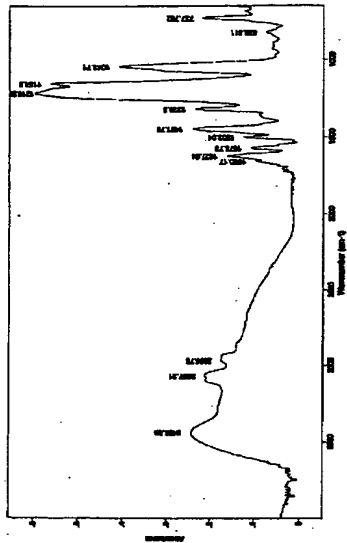
【0019】上述のスルホン酸基含有ジカルボン酸は、芳香族系ジカルボン酸中に1個または2個のスルホン酸基を含有するものを選択することができるが、具体例としては、例えば、2,5-ジカルボキシベンゼンスルホン酸、3,5-ジカルボキシベンゼンスルホン酸、4,6-ジカルボキシ-1,3-ベンゼンジスルホン酸、2,5-ジカルボキシ-1,4-ベンゼンジスルホン酸、4,4'-ジカルボキシ-2,2'-ビフェニルジスルホン酸などのスルホン酸含有ジカルボン酸としては、ナトリウム、カリウムなどのアルカリ金属塩や、アンモニウム塩などをあげることができる。スルホン酸含有ジカルボン酸の構造は特にこれらに限定されることはない。スルホン酸含有ジカルボン酸はそれら単独だけでなく、スルホン酸基を含有しないジカルボン酸とともに共重合の形で導入することができる。スルホン酸基を含有するジカルボン酸の純度は特に制限されるものではないが、98%以上が好ましく、99%以上がより好ましい。スルホン酸基を含有するジカルボン酸を原料として重合させたポリベンズイミダゾールは、スルホン酸基を含有しないジカルボン酸を用いた場合に比べて、重合度が低くなる傾向が見られるため、スルホン酸基を含有するジカルボン酸であるだけ純度が高いものを用いることが好ましい。

【0020】上記スルホン酸基含有ジカルボン酸とともに使用できるジカルボン酸例としては、テフタル酸、イソフタル酸、ナフタレンジカルボン酸、ジフェニルエーテルジカルボン酸、ジフェニルスルホンジカルボン酸、ビフェニルジカルボン酸、ターフェニルジカルボン酸、2,2-ビス(4-カルボキシフェニル)ヘキサフルオロプロパン等ポリエステル原料として報告されている一般的なジカルボン酸を使用することができ、ここで例示したものに限定されるものではない。スルホン酸基含有しないジカルボン酸をスルホン酸基を含有するジカルボン酸とともに使用する場合、平均値としてスルホン酸基は上記式(1)におけるArあたり0.5個以上含

【図1】



【図3】



フロントページの続き

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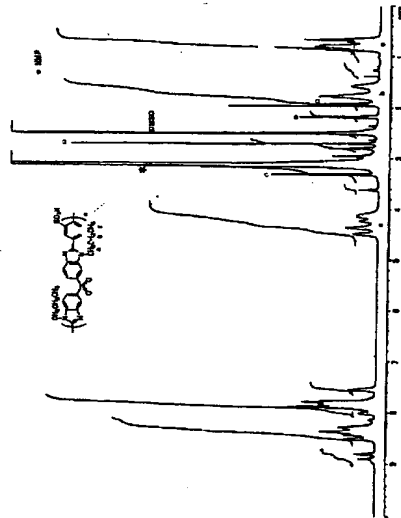
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テ-コ-ド (参考)

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【図2】



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